Sodium Arsenite as a Debarking Agent for Hemlock Trees Causes Serious Loss of Tannin in the Bark[1]

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Sodium arsenite used as a debarking agent for hemlock trees causes a loss of about 30 per cent of tannin in the bark. The effect is not localized but is distributed throughout the height of the tree. Results of the study indicate a need to investigate other debarking chemicals and methods of application.

HAND PEELED BARK from eastern hemlock trees has been an important source of vegetable tannin in North America for more than 100 years. In the early days hemlock trees were cut down for the sole purpose of recovering the bark. Many tanneries sprang up in the proximity of large stands of eastern hemlock. As these stands were exhausted and it became too costly to transport the bark great distances, many of these closed until today we find very few tanneries leaching their own bark.

The amount of tannin produced from hemlock bark is small compared with the amount of tannin derived at present from chestnut wood (our main domestic source) in this country. However, it is desirable to develop new domestic sources of tannin because practically all of the virgin stands of chestnut have been killed by blight.

Confronted with this situation and the fact that close to 90% of the vegetable tannin used in this country must be imported, our national defense authorities place vegetable tannin high on the list of critical materials necessary for a successful war effort.

In order to increase the domestic production of tannin, investigations have been made of such materials as barks from the Florida scrub oaks and the mixed oaks of the Tennessee Valley, canaigre roots from the southwest, barks of hemlock and Douglas-fir from the Pacific Coast. To the foregoing should be added a research project now underway to determine the feasibility of producing hemlock tannin extract from wastes of the logging and pulping industries in the Upper Peninsula of Michigan.

As has already been indicated, the cost of delivering bark to the tannery or extract plant is one of the most important factors governing its continued use as a source of vegetable tannin. Practically all hemlock bark used in the United States today comes from the peeling of logs used for pulp by paper mills in Northern Michigan and Wisconsin. The peeling season in this area for eastern hemlock and other pulpwood species, when bark may be easily removed, is limited to a maximum of three months, usually from mid-May to the middle of August. This time limitation for hand peeling increases the cost of producing the bark.

Within the last 17 years there has been considerable practical experimentation in Canada and the United States on the application of chemicals to living trees to extend and fix easy peeling characteristics. A systematic study of the whole chemical debarking problem, sponsored by industry, has been underway for the past several years at the State University of New York College of Forestry, Syracuse, New York (1).[2]

The results of these practical experiments at Syracuse and by private companies have shown such good promise that it is felt that chemical debarking tchniques will be adopted by a number of firms producing pulpwood. The chemical most commonly used at present in debarking treatments is a 40% solution of sodium arsenite.

The advantages of chemical debarking have been listed as follows (2): "The treatment of standing forest trees with sodium arsenite makes it possible . . . to produce pulpwood almost the year around. Instead of felling and then peeling with axe and spud 2 or 3 cords per day, one man can girdle and treat 10 to 20 cords per day during the sap-peeling season from mid-May until late July. The sodium arsenite kills the tree and after three or four months causes the bark to loosen . . . Treated trees can be felled, yarded and barked up when farm labor is not busy with regular farm work . . . Even in times of poor demand, many pulpwood companies will buy peeled wood when they will not buy rough wood." Other advantages depend upon the fact that the owner or forester can select at the time of the treatment the trees that should be cut.

The same author lists the disadvantages as follows: "Sodium arsenite is poisonous and care must be used in handling it. Wood treated in 1954 cannot be harvested as peeled wood until late fall or the spring of 1955. Not all pulpwood companies buy peeled wood. Sodium arsenite does not guarantee 100% peeled wood. Hand peeling will often be required."

A possible disadvantage not listed above is the effect of the treatment upon the tannin of oak or hemlock barks when used for the production of tanning extracts. Preliminary analyses of barks from treated and untreated trees were made to determine this point.

[1] A contributed paper.

[2] Numbers in parentheses refer to literature cited.

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Experimental Procedure

Samples of bark were obtained from treated and untreated oak trees which were fairly comparable. The bark from the untreated trees had a tannin content of 12.4% and that from the treated trees had 7.9% tannin. This was strong evidence of tannin destruction, but it was not conclusive because the tannin content of the treated bark before treatment was not known. Further, assuming that the loss was as indicated, it could not be determined whether the loss was caused by girdling alone or was caused by the arsenic treatment.

To determine these points, a collaborative experiment was carried out between the Forest Products Research Division of the Michigan College of Mining and Technology, and the Hides, Tanning Materials and Leather Section of the Eastern Utilization Research Branch of the U. S. Department of Agriculture.

Results

On July 2, 1953, with the aid of two timber cruisers employed by the Marathon Corporation, 20 hemlock trees were chosen in the test area (Point Abbaye, Baraga County, Michigan) ranging in diameter at breast height from 14 inches to 22 inches (average d.b.h.—17 inches). Each tree was girdled with an axe, the bottom of the girdle being an average of 3.3 feet above the ground. The girdles averaged 6-1/2 inches in width. The bark from each girdle was carefully collected and bagged. A number was painted on each tree with white marking paint.

On the following morning, a 40% sodium arsenite solution was applied to the ten even-numbered trees. This solution labeled Atlas "A" sodium arsenite was purchased already prepared from the Chapman Chemical Company (Boundbrook, New Jersey).[3] This solution contains 4 pounds of arsenic trioxide per gallon.

As can be seen in Figure 1, the solution is carried in a portable knapsack tank to which air pressure is applied by a pump (about 2 pounds pressure was used) forcing the liquid through the spray hose into the handle of the brush. A spring valve in the hose releases as much solution as desired. Considerable care is given to be sure the girdled section is fully covered by the solution, particularly the upper edge. From the experience of the Marathon Corporation, one gallon of solution is required for every 20 cords of pulpwood treated.

The bark samples were spread on screen bottomed trays especially built for this purpose and stacked to dry outside the Forest Products Research Division building at Houghton, Michigan, under a lean-to shelter to prevent rain from leaching tannin from the bark. By August 1 the moisture content of several samples averaged 16.9 per cent on a dry basis. Within two weeks all samples were weighed and shipped to the Eastern Regional Research Laboratory for tannin analysis.

Inspection of the test plot on August 21, 1953, showed that five of the trees that had been treated were dead and on the remaining five few green needles remained.

[3] In furnishing the name of the company mentioned, it is understood that the U. S. Department of Agriculture does not in any way guarantee their product, nor is it recommended in preference to others not mentioned.

Table 1.—EFFECT OF GIRDLING ONLY AND GIRDLING PLUS TREATMENT WITH SODIUM ARSENITE

Tree No.	Sol. Extractives % 1st Girdling	Sol. Extractives % After 1 Year	Non-Tannin % 1st Girdling	Non-Tannin % After 1 Year	Tannin % 1st Girdling	Tannin % After 1 Year	Purity = Tan/Sol. Ext. x 100 1st Girdling	Purity = Tan/Sol. Ext. x 100 After 1 Year
TREES GIRDLED ONLY AT BREAST HEIGHT			A′	B′	A	B		
1	25.09	26.54	8.75	9.88	16.34	16.66	65.13	62.77
3	22.03	25.30	8.20	9.44	13.83	15.86	62.78	62.69
5	23.57	23.03	8.63	8.34	14.94	14.69	63.38	63.79
7	23.14	25.26	8.38	9.30	14.76	15.96	63.79	63.18
9	24.33	26.71	8.56	9.65	15.77	17.06	64.82	63.87
11	24.93	26.69	8.52	9.73	16.41	16.96	65.82	63.54
13	25.31	27.56	9.52	10.22	15.79	17.34	62.39	62.92
15	25.49	27.52	9.22	9.70	16.27	17.82	63.83	64.75
17	24.66	26.22	9.69	10.16	14.97	16.06	60.71	61.25
19	27.63	30.21	9.98	9.85	17.65	20.36	63.88	67.39
Avg.	24.62	26.50	8.95	9.63	15.67	16.87	63.65	63.62
TREES GIRDLED AND TREATED WITH SODIUM ARSENITE			C′	D′	C	D		
2	26.43	20.65	8.34	6.24	18.09	14.41	68.44	69.78
4	24.43	18.33	8.51	5.47	15.92	12.86	65.17	70.16
6	26.21	17.34	9.93	5.70	16.28	11.64	62.11	67.13
8	28.13	20.67	9.79	6.17	18.34	14.50	65.20	74.14
10	29.60	21.32	10.33	6.67	19.27	14.65	65.10	68.71
12	27.41	16.97	9.98	5.88	17.43	11.09	63.59	65.35
14	27.05	18.45	9.68	5.56	17.37	12.89	64.21	69.86
16	26.62	19.39	9.99	5.94	16.63	13.45	62.47	69.37
18	20.79	14.72	8.25	4.93	12.54	9.79	60.32	66.51
20	18.79	14.33	6.85	4.41	11.94	9.92	63.54	69.23
Avg.	25.54	18.22	9.16	5.70	16.38	12.52	64.02	68.62

Fig. 1.—Method of applying the arsenite solution.

Table 2.—EFFECT OF GIRDLING AND TREATMENT ON BARK 20 FEET ABOVE GIRDLING POINTS*

Tree No.	Soluble Extractive %	Non-Tannin %	Tannin %	Purity = Tan/Sol. Ext. x 100
TREES GIRDLED ONLY		E′	E	
1	23.63	10.47	13.16	55.69
3	20.40	8.89	11.51	56.42
5	20.80	7.86	12.94	62.21
7	21.38	8.51	12.87	60.20
9	23.65	9.85	13.80	58.35
11	25.56	11.90	13.66	53.44
13	23.02	9.47	13.55	58.86
15	24.78	9.90	14.88	60.05
17	26.03	12.28	13.75	52.82
19	28.89	12.27	16.62	57.53
Avg.	23.81	10.14	13.67	57.56
TREES GIRDLED AND TREATED WITH SODIUM ARSENITE		F′	F	
2	15.92	6.77	9.15	57.49
4	14.07	4.88	9.19	65.32
6	15.54	6.19	9.35	60.17
8	17.71	6.22	11.49	64.88
10	17.99	6.11	11.88	66.04
12	14.87	5.93	8.94	60.12
14	15.05	5.64	9.41	62.52
16	17.11	5.96	11.15	65.17
18	13.49	5.31	8.18	60.64
20	14.81	4.56	10.25	69.21
Avg.	15.66	5.76	9.90	63.16

*Trees were sampled only at end of test.

It has been determined that best results can be obtained on treated trees by allowing them to stand over winter before harvesting. The alternate freezing and thawing and swaying of the trees helps to loosen much of the bark. Thus, in the case of this experiment, it was decided to allow one year to elapse before taking additional bark samples.

The Marathon Corporation had retained a logging jobber to cut their pulpwood on Point Abbaye and they arranged with him to have our 20 test trees cut down on July 8, 1954. One of the authors was present when the hemlock was cut down and supervised the taking of additional samples from each tree. The first sample in each case was another girdle section of bark immediately above that removed on July 2, 1953. These sections were about 9 inches in width. The second sample from each tree was obtained 20 feet up the trunk from the top edge of the lower girdle just removed. A larger width of girdle was taken here, averaging about 15 inches.

Every sample taken from the treated trees came off the trunk very easily. Those from the girdled but untreated trees came off less readily, and in the case of No. 5 tree the bark was very tight and difficult to peel.

All of the bark samples were again carefully collected and dried on screens as was done a year previously. When weighed and shipped to the Eastern Regional Research Laboratory, the moisture content on three samples averaged 17.69 per cent.

All bark samples were analyzed at the laboratory by the official methods of the American Leather Chemists Association (3). The results of these analyses are shown in Tables 1 and 2 and a summary and analysis of the results in Table 3 (4).

Discussion

It will be seen from Table 1 that in every case where a tree was girdled and treated with sodium arsenite, there has been an appreciable loss of tannin. As shown in Table 3, this loss was 30.97 ± 7.88% of the tannin in the bark originally. There was a loss of 45.47 ± 8.37% of the non-tannin. This disproportionate loss of non-tannin as compared with tannin has raised the purity of the bark.

Table 2 shows that there has been a large loss of tannin in the bark 20 feet above the girdling point on trees treated with the arsenite. The trees were not sampled at this point originally and therefore the exact loss of tannin cannot be determined. If we asume that the average difference in per cent tannin between breast height and 20 feet was similar for the two lots of 10 trees at the beginning of the experiment, Table 3 indicates a loss of 25.80 ± 10.42% of the tannin at the 20-foot height due to the use of sodium arsenite. This is of the same order of magnitude as the loss at the girdling point.

Where the trees were girdled only and not treated, there has been an increase in tannin in every case but one, as shown in Table 1. As shown in Table 3 this increase is significant and amounts to 7.66 ± 3.75% of the tannin. This may be caused by an increase in tannin content during the year. It might also be caused by leaching of the bark during rain storms, and the accumulation of soluble matter near the base where the sample was taken. If this same leaching and deposition of tannin also took place in the treated trees, the tannin content of these samples at the end of the test would also be higher in the same proportion. Therefore, the loss of tannin would actually be somewhat higher than that shown in Table 1. However, this is of only minor importance.

The arsenic contents of the bark samples from the treated trees were: breast height–15 to 40 parts arsenic per million parts of bark; 20 foot height—2 to 3 p.p.m. It seems highly unlikely that the chemical effects of this amount of arsenic on tannin would be significant. We must probably look elsewhere for the cause of the destruction. However, it would seem desirable to determine the effects of other materials proposed for debarking, such as sodium monochloracetate, chloracetaldehyde, or ammonium sulfamate. It would also be desirable to investigate other factors, such as concentration of solution, and length of time between application and felling.

Table 3.—ANALYSIS OF RESULTS*

Columns Compared	Variables	$\overline{X}_1$	$\overline{X}_2$	S_1	S_2	t*
A vs B	Tannin with time (one year)	15.67	16.87	1.082	1.514	2.04
C vs D	Tannin with time + sodium arsenite	16.38	12.52	2.403	1.831	4.04
B vs E	Tannin with height† (20 feet)	16.87	13.67	1.514	1.346	4.99
D vs F	Tannin with height‡ (20 feet)	12.52	9.90	1.831	1.230	3.75
$\frac{A-B}{A}$ vs $\frac{C-D}{C}$	Tannin with sodium arsenite	7.66%	23.31%	5.246%	5.70%	12.61
$\frac{A-E}{A}$ vs $\frac{C-F}{C}$	Tannin with sodium arsenite (20 ft.)	12.84	+38.64	4.300	10.256	§
$\frac{A'-B'}{A'}$ vs $\frac{C'-D'}{C'}$	Non-tannin with sodium arsenite	7.87%	37.60%	6.4800%	5.208%	18.87

95% Confidence Units—Net Loss due to Sodium Arsenite

$$\left.\begin{array}{l} \frac{A-B}{A}\ (\text{Tannin}) \pm 3.75\% \\ \frac{C-D}{C}\ (\text{Tannin}) \pm 4.13\% \end{array}\right\} (-7.66 \pm 3.75\%)-(+23.31 \pm 4.13\%) = -30.97 \pm 7.88\%$$

$$\left.\begin{array}{l} \frac{A'-B'}{A'}\ (\text{Non-tannin}) \pm 4.84\% \\ \frac{C'-D'}{C'}\ (\text{Non-tannin}) \pm 3.73\% \end{array}\right\} (-7.87 \pm 4.64\%)-(37.60 \pm 3.73\%) = -45.47 \pm 8.37\%$$

$$\left.\begin{array}{l} \frac{A-E}{A}\ (\text{Tannin—20 ft.})\ 12.84 \pm 3.08 \\ \frac{C-F}{C}\ (\text{Tannin—20 ft.})\ 38.64 \pm 7.34 \end{array}\right\} (+12.84 \pm 3.08)-(38.64 \pm 7.34\%) = 25.80 \pm 10.42\%\|$$

*Critical I 0.01 = 2.878.
†Untreated trees—one year after girdling.
‡Arsenite treated trees—one year after girdling.
§t value invalid because F value is critical.
‖The assumption was made that the average difference in per cent tannin between breast height and 20 feet was similar for the two lots of 10 trees at the beginning of the experiment.

Conclusions

The use of sodium arsenite as a chemical debarking agent for hemlock trees causes a loss of about 30% of the tannin in the bark. The effect is not localized but is distributed throughout the height of the tree. There is a need to investigate other debarking chemicals and methods of application.

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